# Fabrication and activation studies of conducting plastic composite electrodes for redox cells

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## Abstract

Conducting polyethylene (PE) composite material is fabricated by mixing polyethylene with conducting fillers. Electrical, mechanical, permeation and electrochemical studies show that the PE composite is a good electrode matrix material for the vanadium redox battery. Chemical treatment studies on two kinds of PE composites show that the material with a high graphite-fibre content has good electrochemical activity and stability after treatment. Further cyclic voltammetry and SEM investigations indicate that chemical treatment increases the active surface area of the PE composite.

## Introduction

Conductive polymers, or plastics, are promising electrode materials for a large number of industrial electrochemical applications since they offer low-cost, low-weight alternatives to traditional graphite or carbon electrodes, and can be easily moulded into any shape and size [1–8]. Conductive polymers, such as polypyrrole, have good electrical conductivity [9], but are easily attacked by acidic and oxidative electrolytes. In applications such as the vanadium redox battery [10], therefore, conductive polymers are unsuitable for use as electrodes.

Conducting graphite/polyethylene composite electrodes have, however, been successfully used in the vanadium redox cell. Indeed, energy efficiencies of up to 90% have been achieved with Japanese materials in 1 kW prototype batteries [11]. Since these materials are expensive, the objective of the present work is to develop formulations and processes to give a more cost-effective product. In particular, a suitable activation treatment is investigated in order to eliminate the need for a costly graphite mat, or felt, active layer.

The important properties governing the use of materials as electrodes, include: conductivity, mechanical integrity, permeability, electrochemical activity, stability in the electrolyte. These properties have been evaluated in the present study as a function of the composition of the PE/graphite composites. Treatment of the surface of the conducting plastic has also been

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examined with the objective of enhancing the electrochemical activity for redox-cell applications.

## Experimental

### Preparation of composite

The following materials were used in the preparation of the conducting plastic composites:

- Polymer: low density polyethylene powder (LDPE), MFI (17/1200), (MANIS Pty. Ltd., Brookvale 2100, Australia).
- Carbon and graphite products: carbon black: CABOT 'Black Pearl 2000' (Cabot Corporation, Billerica Technical Centre, U.S.A.).
- Graphite powder: LONZA KS-2.5 graphite (LONZA Inc., Fairlawn, U.S.A.).
- Graphite fibre: KUREHA C-203s (Kureha Chemical Industry Co., Ltd., Chuo-ku, Tokyo, Japan).

The ingredients were weighed, poured into a Rheomir 600 internal mixer, heated to 140 °C, and mixed at this temperature for 20 min with a blade speed of 50 r.p.m. The mixture was then removed and placed into square moulds with dimensions $152 \times 152 \times 0.3$ to 2.0 mm. The mould was heated to 140 °C and the mixture left for 30 min. A pressure of 225 kg cm$^{-2}$ was then applied in a Stacy Hydraulics 40 tonne press for 30 min at the same temperature. The pressure was then released and the mould allowed to cool to obtain thin, smooth polyethylene composite sheets.

### Evaluation and properties

#### Resistivity measurements

The ASTM D-991 method was employed for measurement of resistivity. It is well known that the conductivity of the composite plastics will be affected greatly by the type of polymer [12], as well as by the type and particle size of the conducting materials [13–16]. In initial studies of composite development, low density polyethylene powder (LDPE), Black Pearl carbon black (CB), graphite powder (GP) and graphite fibres (GF) were used in various proportions.

#### Permeation measurements

To evaluate the permeability of the materials, a small round cell with a solution pumping system was employed. The conducting plastic sheet was used as a separator between the two electrolyte compartments. One side contained 1 M $V^{3+}$ + 1 M $VO^{2+}$ in 3 M $H_2SO_4$ solution (the mixed electrolyte of the vanadium battery), the other side a 3 M $H_2SO_4$ blank solution. Both solutions were pumped for 18 days, and 5 ml samples were withdrawn periodically from the $H_2SO_4$ compartment. The concentration of vanadium ions in these samples was determined by inductively coupled plasma (ICP) analysis.

*Preparation of electrodes for cyclic voltammetry*

In order to simulate the electrode working conditions during battery operation, a small electrode was fabricated for cyclic voltammetric tests. A piece of graphite felt (diameter 1 cm) and a piece of copper mesh of the same size were heat-pressed onto either side of the composite polyethylene sheet; the felt side was used as the working surface and the copper mesh as the current collector. After rigorous sealing with epoxy resin, the electrode (projected area = 0.785 cm$^2$) was placed into the electrolyte (1 M $V^{3+}$ + 1 M $VO^{2+}$ in 3 M $H_2SO_4$) together with a saturated calomel reference electrode (SCE) and a graphite plate (3 × 4 cm) counter electrode. A PAR 174 potentiostat/galvanostat and its associated equipment were employed for the cyclic voltammetric experiments.

*Evaluation of chemical treatment*

Small rectangular (7 × 1.6 × 10 mm) specimens were cut from each of composites A and B described in Table 1. The samples were firmly fixed to a graphite rod and then sealed in a glass tube with epoxy resin (Fig. 1). Two kinds of electrodes were prepared for each composite; these are designated the 's' and 'e' electrodes. With the 's' electrode, the surface exposed to the electrolyte is the as-prepared, surface of the composite while for the 'e' electrode, the cross section of the composite is exposed to the solution (see Fig. 1). For comparison, a graphite plate electrode with the same surface area was fabricated in the same way.

The chemical treatment solution had the following composition:

$H_2SO_4$ (97%) AR    800 g l$^{-1}$
$K_2Cr_2O_7$ AR       30 g l$^{-1}$
$H_2O$                the rest

The effectiveness of the chemical treatment was evaluated using cyclic voltammetry and scanning electron microscopy.

## Results and discussion

*Effect of composition on resistivity*

Figure 2 and Table 2 give a comparison of the resistivity of the three materials used in the same proportions in the conducting composite mixture.

TABLE 1

Composition and resistivity of composite PE used in chemical treatment studies

| Samples | Composition (%) | Resistivity (Ω cm) |
|---------|-----------------|--------------------|
| A | LDPE 50 CB 25 GF 25 | 0.13 |
| B | LDPE 25 GF 75 | 0.17 |

COMPRESS DIRECTION

WORKING SURFACE OF 's' ELECTRODES

COMPOSITE PE SHEET

WORKING SURFACE OF 's' ELECTRODES

(a)

graphite rod

epoxy resin

glass tube

electrode material

(b)

SECTION A - A

glass tube
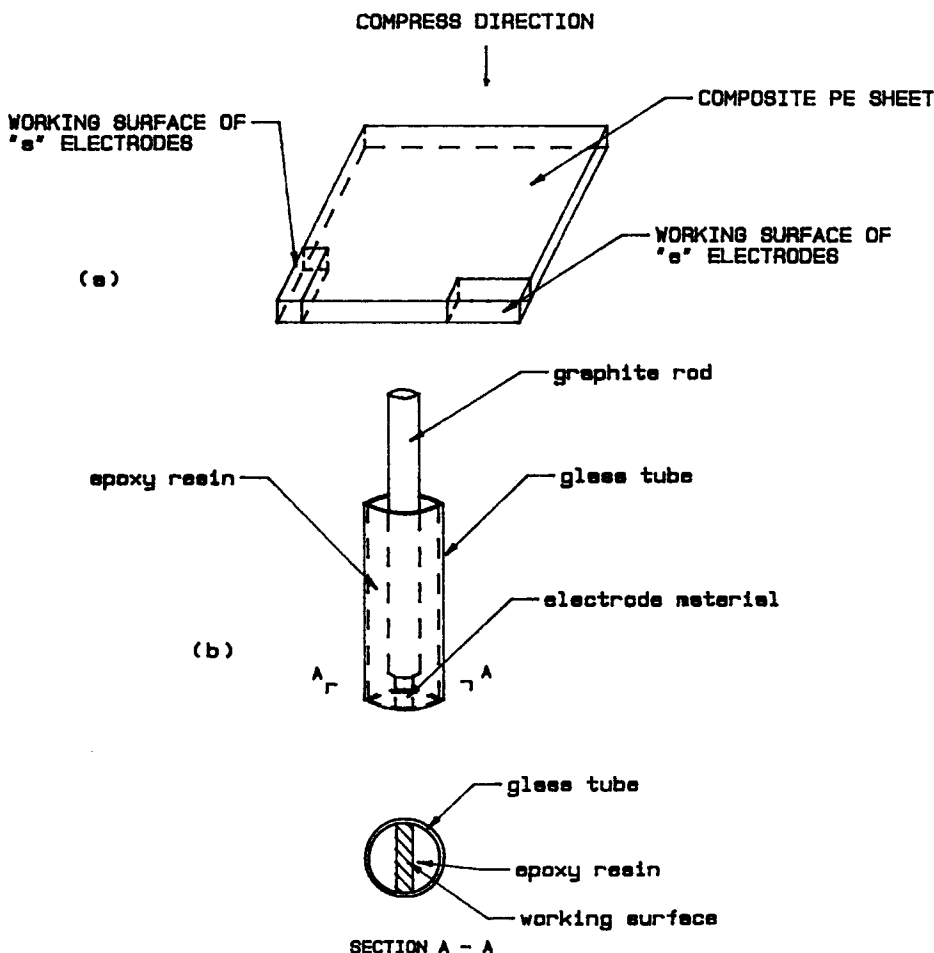
epoxy resin

working surface

Fig. 1. Schematics of composite conducting plastic sheet and electrodes for chemical treatment studies: (a) composite sheet; (b) electrode construction.

It is clear that, for the same loading, the inclusion of graphite powder gives rise to a less conductive composite than the other materials. The dramatic decrease in resistivity (7 orders of magnitude) when the graphite fibre content was increased from 10% to 20% is attributed to the development of an electrical network for the passage of current through the composite [17]. The loading of BP carbon black has a less dramatic effect on resistivity. Further experiments showed that the combination of graphite fibre and carbon black gave better electrical properties (Table 3) than graphite fibre alone.

This combination of filler leads to an enhancement of the conductivity. Additional formulations were tested and samples were prepared with the aim of reducing resistivity to less than 1 $\Omega$ cm. The following formulation was found to have a resistivity of around 1 $\Omega$ cm: 70% high density polyethylene, 15% BP, 15% GF. Even lower resistivity could be obtained with higher carbon
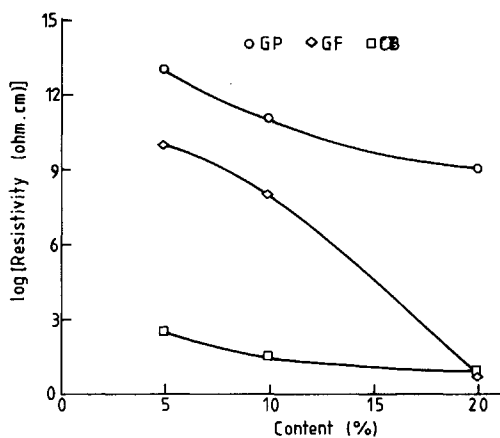
Fig. 2. Influence of conducting filler control on the resistivity of PE composites (GP = graphite powder, CB = BP = Black Pearl carbon black, GF = graphite fibre).

TABLE 2

Resistivity of materials in same proportions

| Content (%) | Materials | Resistivity ($\Omega$ cm) |
|---|---|---|
| 5 | GP | $> 10^{12}$ |
| | GF | $1 \times 10^{10}$ |
| | BP | $3.13 \times 10^2$ |
| 10 | GP | $3.3 \times 10^{10}$ |
| | GF | $2.4 \times 10^8$ |
| | BP | $3.26 \times 10$ |
| 20 | GP | $3.3 \times 10^9$ |
| | GF | 4.9 |
| | BP | 8.2 |

TABLE 3

Resistivity of materials in different proportions

| Composition | Resistivity ($\Omega$ cm) |
|---|---|
| 80% PE + 20% BP 8.2 | 8.2 |
| 80% PE + 20% GF 4.9 | 4.9 |
| 80% PE + 10% BP + 10% GF | 1.6 |

loading as shown in Table 1, although the mechanical properties of the composite tended to degrade considerably.

### Mechanical properties

As described above, a combination of carbon black (BP) and graphite fibre (GF) in the ratio 1:1 (total fraction being 30% of the composite)
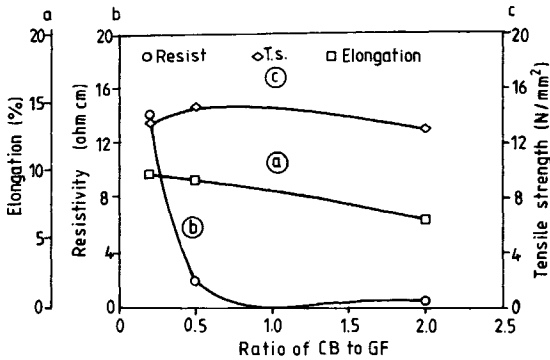
Fig. 3. Influence of Black Pearl carbon black (CB) on resistivity and mechanical properties of PE composites.
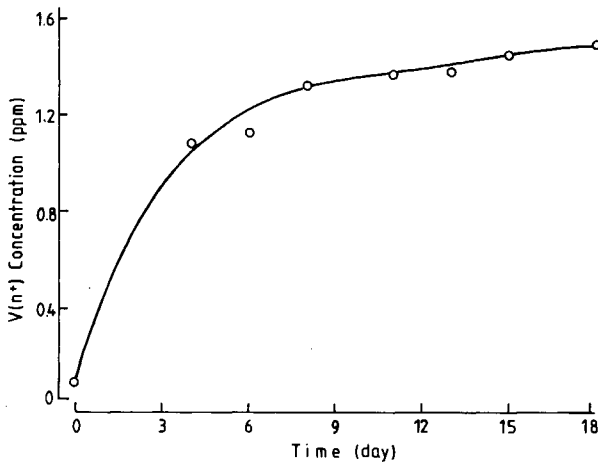


Fig. 4. Permeation behaviour of composite PE Sheet (70% PE, 15% BP, 15% GF).

produced a composite with a resistivity of 1 $\Omega$ cm. Further experiments showed that even lower resistivities could be obtained by increasing the ratio of BP to GF, as illustrated in Fig. 3. Increasing the proportion of BP, however, also resulted in a deterioration in the mechanical properties of the composite, i.e., both tensile strength and elongation decreased (Fig. 3). In these experiments, the total percentage of BP and GF in the composite was 30%. Varying both the total carbon content and the ratio of BP to GF may thus allow a reduction in resistivity to be achieved without a decrease in the mechanical properties.
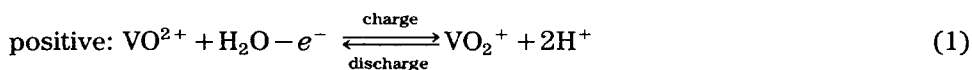
*Permeation*

When employed in electrode fabrication for redox-cell applications, an electrochemically active layer is bonded to the top and a current collector (normally a metal foil or mesh) to the back of the composite sheet. If the

thin composite polyethylene sheets have a high permeability, the electrolyte (which in the present system is vanadium ions in sulphuric acid) will pass through the sheet and attack the current collector, and also possibly leak from the battery during operation. The permeation behaviour is therefore one of the most important performance characteristics of the carbon/polyethylene composites. From the results shown in Fig. 4, it appears that the permeation rate of vanadium ions is negligible for material of composition70% HDPE, 15% BP, 15% GF.

*Cyclic voltammetry*

The following reactions occur during charging and discharging of the vanadium redox battery:

charging:

$$\text{positive: } VO^{2+} + H_2O - e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} VO_2{}^+ + 2H^+ \tag{1}$$

$$\text{negative: } V^{3+} + e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} V^{2+} \tag{2}$$

A good electrode for this battery should have high electrochemical activity for the above reactions, and also be stable in the electrolyte during charge/ discharge cycling. Figure 5 shows cyclic voltammograms obtained for a conducting plastic electrode (composite 70% PE, 15% BP, 15% GF) onto which a piece of FMI graphite felt was bonded. The four peaks corresponding to the above forward and reverse electrode reactions of the four vanadium species can be observed (peaks A and B: $V(IV) \rightleftharpoons V(V)$; peaks C and D:



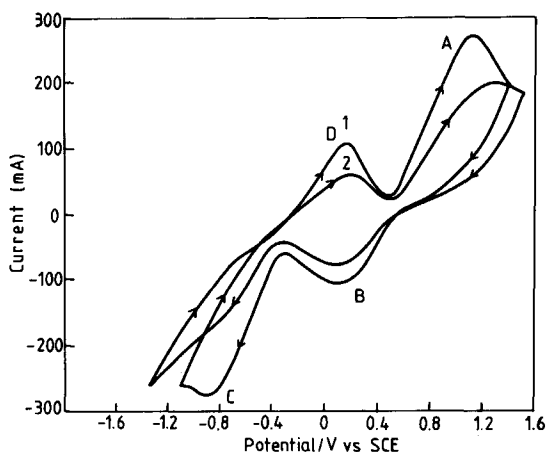Fig. 5. Cyclic voltammogram for composite PE (projected area = 0.785 cm$^2$) and graphite electrode (area = 0.785 cm$^2$) in (1 M V(III) + 1 M V(IV))/3 M H$_2$SO$_4$ solution, (1) graphite felt bonded to PE composite (70% PE, 15% BP, 15% GF); (2) graphite felt bonded to graphite rod (scan rate = 100 mV s$^{-1}$).
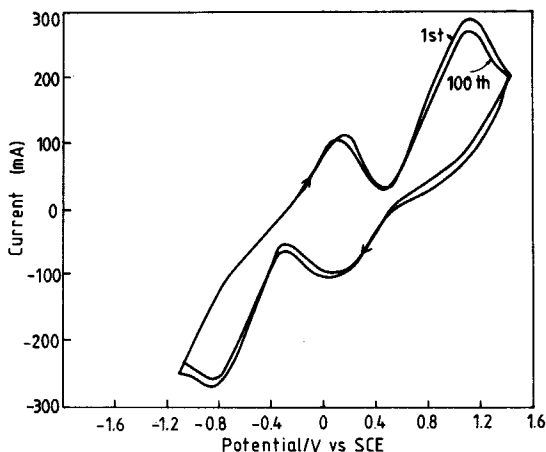
Fig. 6. Cyclic stability test for composite PE/graphite felt electrode (scan rate = 100 mV s$^{-1}$).

V(III) $\rightleftharpoons$ V(II). This indicates that the graphite-felt-bonded composite poly-ethylene electrode structure has good electrochemical activity in the electrolyte. Curve 2 illustrates the electrochemical behaviour of a graphite rod electrode of similar size with the same graphite felt bonded to the surface. From the two curves, it appears that the composite polyethylene is a better electrode substrate material. This is probably due to the lower contact resistance between the graphite felt and conducting plastic substrate which can be achieved by heat pressing. Figure 6 gives further cyclic voltammetric results that demonstrate the stability of the electrode during operation. After 100 cycles, only a negligible change in the electrode behaviour was recorded. Thus, these materials have excellent long-term characteristics for the vanadium battery applications. Because of the high surface area, high conductivity and reactivity of the graphite felts, very high cell and battery efficiencies have been achieved with these electrodes.

*Chemical treatment*

Significant cost reduction could be achieved by total elimination of the felt and direct activation of the conducting plastic surface. The surface of the conducting composite polyethylene, although electrically conductive, is, however, covered by the bonding plastic which reduces both the surface hydrophilicity and the reaction area. The purpose of chemical treatment is to increase the surface hydrophilicity, the reactive surface area and, if possible, the active sites or functional groups that can catalyse the electrochemical reactions. Polyethylene is very stable to most chemicals and solvents; only strongly oxidative and acidic solutions can attack its surface. A chromate–sulphuric acid system was therefore employed for surface treatment.

*Influence of treatment time*

The prepared electrodes were polished, successively, with 120, 320 and 400 sand paper (the latter for the 'e' and graphite electrodes only), cleaned

with acetone and water, and then etched in the hot (65 °C) chemical treatment solution for various time periods. The cyclic voltammograms for the two kinds of composite polyethylene electrodes and for graphite electrodes are shown in Figs. 7–9, respectively. Further details are given in Table 4, and Figs. 10 and 11. In the Tables, $I_{p1}$ and $I_{p2}$ refer, respectively, to the peak current of the two electrode reactions: $V(IV) - e^- \rightarrow V(V)$ (peak A in Fig. 5), and $V(III) + e^- \rightarrow V(II)$ (peak C in Fig. 5); $\Delta E_{p1}$, $\Delta E_{p2}$ refer to the peak potential separations of the two redox couples, respectively.

The data (Table 4, Figs. 7, 8) show that both composite electrodes exhibit an increase in peak current with increasing treatment time. This is probably due to an increase in the surface hydrophilicity as well as to increased exposure of the conductive material, which was initially covered by bonding polyethylene. Both effects would enhance the vanadium ion reactions. Comparing the data in Figs. 7–11 and Table 4, it is clear that the effect of the short-time treatment on the peak current is more pronounced in the case of the PE2525 than the PE75 electrodes. This is probably due to the fact that carbon black is more conductive than graphite fibre. With longer treatment times, however, the effect on peak current is greater with the PE75 electrodes (cf. Figs. 10 and 11). An explanation for this reverse in behaviour may lie in the fact that more of the graphite fibres are exposed so that the surface area of the PE75 electrode becomes greater than that of the PE2525 composite. For the same composite, however, the 'e' electrodes are seen to produce a higher reacting current. This can be attributed to the graphite fibres having
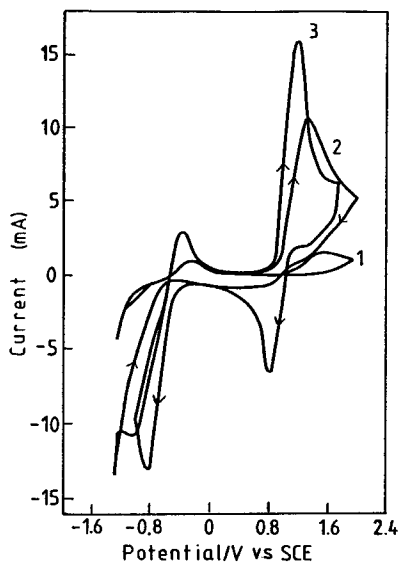


Fig. 7. Cyclic voltammograms for PE2525 composite electrode in vanadium solution (same as Fig. 5): (1) untreated; (2) 5 min treated; (3) graphite (scan rate = 100 mV s$^{-1}$).
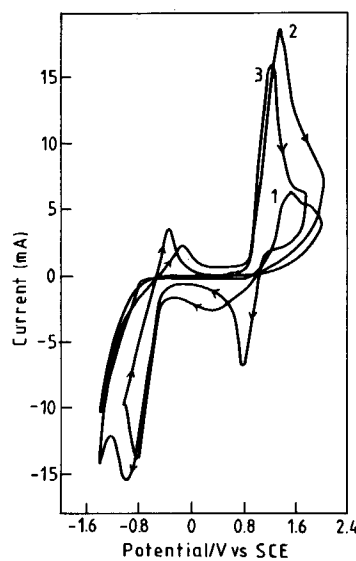
Fig. 8. Cyclic voltammograms for PE75 composite electrode in vanadium solution (same as Fig. 5): (1) untreated: (2) 5 min treated; (3) graphite (scan rate = 100 mV s$^{-1}$).
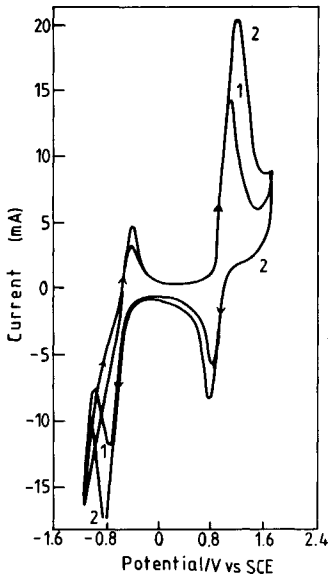
Fig. 9. Cyclic voltammograms for graphite electrode in vanadium solution (same as Fig. 5): (1) untreated; (2) 5 min treated (scan rate = 100 mV s$^{-1}$).
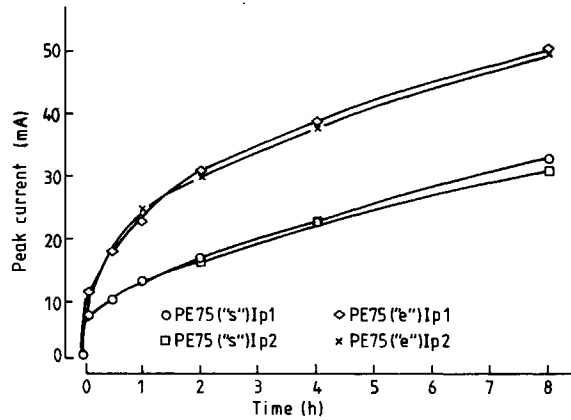
Fig. 10. Effect of treatment time on peak current for PE2525 composite electrode.
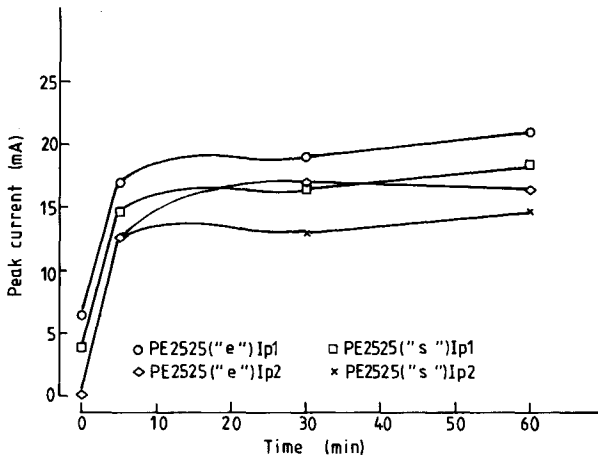


Fig. 11. Effect of treatment time on peak current for PE75 composite electrode.

a higher electrochemical activity in the cross-sectional direction compared with their surface.

In the case of the graphite electrode (see Fig. 9 and Table 4), a 5 min etch caused the peak current to increase but longer treatment yielded no further improvement. Since the graphite electrode has a constant surface area, only the first etch would be expected to increase the surface hydrophilicity.

TABLE 4

Influence of treatment time on the behaviour of different electrodes

| Time (min) | $I_{p1}$ (mA) | $I_{p2}$ (mA) | $\Delta E_{p1}$ (V) | $\Delta E_{p2}$ (V) |
|---|---|---|---|---|
| Electrode PE2525 ('e' electrode) | | | | |
| 0 | 6.40 | | | |
| 5 | 17.00 | 12.60 | 1.00 | 0.85 |
| 30 | 19.00 | 17.00 | 0.90 | 0.64 |
| 60 | 21.00 | 16.50 | 0.60 | 0.52 |
| Electrode PE2525 ('s' electrode) | | | | |
| 0 | 4.00 | | | |
| 5 | 14.60 | 12.40 | 0.60 | 0.52 |
| 30 | 16.40 | 13.00 | 1.32 | 0.52 |
| 60 | 18.40 | 14.60 | 0.84 | 0.52 |
| Electrode PE75 ('s' electrode) | | | | |
| 0 | 0.60 | | | |
| 5 | 7.00 | 7.00 | 0.52 | 0.72 |
| 30 | 9.60 | 9.40 | 0.68 | 0.68 |
| 60 | 12.40 | 12.40 | 0.68 | 0.68 |
| 120 | 16.00 | 15.60 | 0.68 | 0.68 |
| 240 | 22.00 | 22.00 | 0.88 | 0.88 |
| 480 | 32.00 | 30.00 | 1.20 | 1.08 |
| Electrode PE75 ('e' electrode) | | | | |
| 0 | 1.60 | | | |
| 5 | 10.80 | 10.80 | 0.48 | 0.80 |
| 30 | 17.00 | 17.00 | 0.60 | 0.68 |
| 60 | 22.00 | 23.80 | 0.60 | 0.64 |
| 120 | 30.00 | 29.20 | 0.60 | 0.68 |
| 240 | 38.00 | 37.00 | 0.72 | 0.84 |
| 480 | 49.60 | 48.80 | 1.00 | 1.00 |
| Graphite electrode | | | | |
| 0 | 15.00 | 13.00 | 0.32 | 0.40 |
| 5 | 22.00 | 17.00 | 0.40 | 0.40 |
| 30 | 22.00 | 18.00 | 0.64 | 0.48 |
| 60 | 26.00 | 20.80 | 0.64 | 0.48 |
| 90 | 24.00 | 19.20 | 0.64 | 0.48 |

The general trends in peak current versus treatment time for the two kinds of composite plastic electrodes are summarized in Figs. 10 and 11.

*Cyclic stability*

The PE2525 and PE75 electrodes were continuously cycled between their positive and negative potential limits ($+2.0$ V and $-1.2$ V, respectively) to study their stability. The composite with 25% graphite fibre and 25% carbon black is not electrochemically stable; the peak current decreases with cycle number (Fig. 12). This is probably caused by the carbon black particles being removed from the surface and, thereby, giving rise to a reduction in the reactive surface area. The composite with 75% graphite fibre (and the
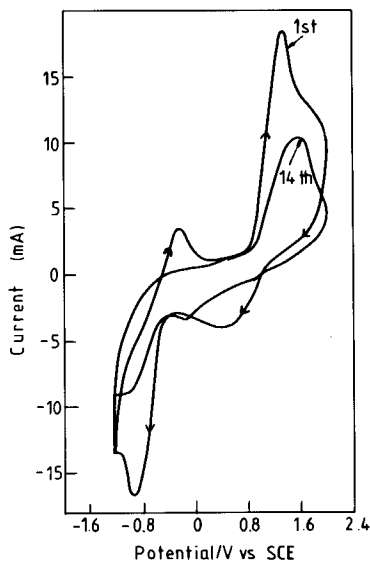
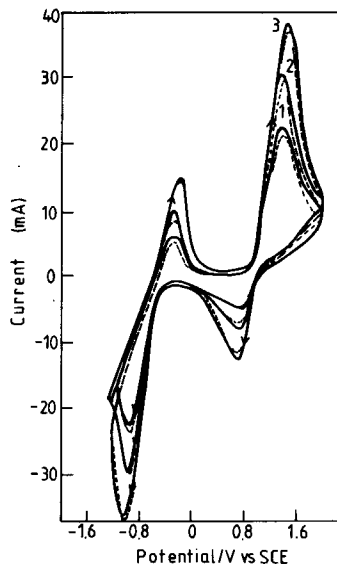Fig. 12. Cyclic stability test of treated PE 2525 composite electrode (30 min, 65 °C); scan rate = 100 mV s$^{-1}$.

Fig. 13. Cyclic stability test of treatment composite electrode: (1) 1 h; (2) 2 h; (3) 4 h. All treated at 65 °C (scan rate = 100 mV s$^{-1}$). Solid line: 1st cycle; broken line: 10th cycle.
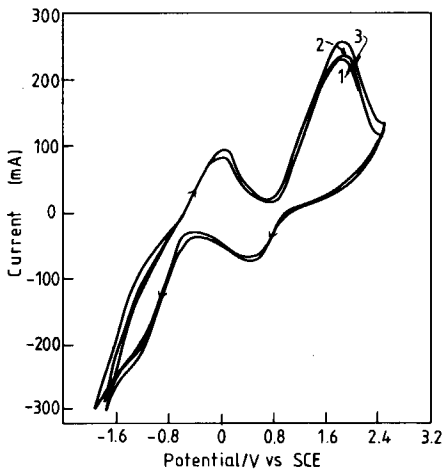


Fig. 14. Cyclic voltammogram for PE composite bonded with graphite felt: (1) untreated; (2) 5 min at 65 °C; (3) 40 min at 65 °C (scan rate = 100 mV s$^{-1}$).

graphite plate electrode) exhibited very good stability during cycling, however (Fig. 13), and would therefore be more suitable for use as an electrode material.

*Mechanism of chemical treatment*

The treatment solution employed in this study is a highly oxidizing acidic solution. Its function could be, simply, to increase surface area and hydrophilicity, or alternatively to create functional groups or active sites for the vanadium reactions. To determine which effect is more important, a graphite felt electrode (bonded onto a 70% PE, 15% BP, 15% GF conducting polyethylene sheet) was subjected to the treatment process and then tested by cyclic voltammetry. Because the felt electrode has a high and constant surface area, if the treatment creates functional groups or active sites, the peak current should increase significantly. The results in Fig. 14, however, show that there is little difference in the peak current before and after treatment.
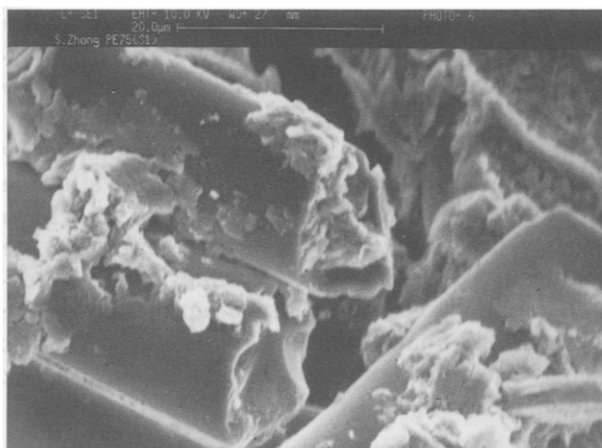


(a)
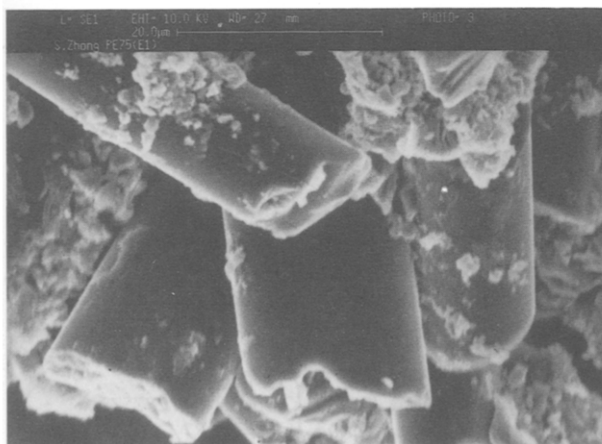


(b)

Fig. 15. Electron micrographs of treated (4 h) PE75 composite material: (a) surface direction; (b) cross section.

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We can thus conclude that the present treatment does not increase the number of active sites on the electrode surface, but rather increases the surface area and surface hydrophilicity of the composite polyethylene electrodes. Further evidence is given by the SEM photographs in Fig. 15. These demonstrate that, after treatment, more of the graphite fibres are exposed on the surface, only a small part of surface still being covered by the polyethylene. This causes the peak current to increase significantly after treatment.

## Conclusions

Conducting plastic materials with resistivities as low as 0.13 $\Omega$ cm can be fabricated from mixtures of carbon black, graphite fibre and low density polyethylene. Chemical treatment of graphite fibre-based composite polyethylene can result in a surface area enhancement and improved reactivity for the vanadium-ion redox reactions.

Whilst carbon-black composite polyethylene is not an electrochemically stable material after treatment, graphite fibre-based conducting polyethylene is. Although significant improvements in the effective surface area have been achieved with surface treatment of these materials, further research on the activation of the exposed graphite fibres is required to achieve better electrochemical activity for the vanadium reactions. Direct activation of the conducting plastic surface will then eliminate the need for the graphite felt and dramatically reduce the cost of electrodes used in the vanadium redox battery, while maintaining a high efficiency.

## Acknowledgements

## References

1 K. Kordesch, J. Gsellmann, S. Jahangir and M. Schautz, *Proc. Symp. Porous Electrode: Theory and Practice, Detroit, MI, 1984*, Vol. 84-8, Electrochemical Society, Pennington, NJ, pp. 163–190.
2 O. Hiroyasu and K. Akito, *Japan Kokai Tokyo Koho JP 88/40261.*
3 O. Hiroyasu and K. Akito, *Japan Kokai Tokyo Koho JP 88/40267.*
4 O. Hiroyasu and K. Akito, *Japan Kokai Tokyo Koho JP 88/40268.*
5 K. Minru, M. Kinoo and S. Kazuharu, *Japan Kokai Tokyo Koho JP 87/287572.*
6 K. Minru, M. Kinoo and S. Kazuharu, *Japan Kokai Tokyo Koho JP 87/276761.*
7 B. S. Eaker and M. G. Klein, *US Patent No. 3 898 099.*
8 C. Herscovici, *US Patent No. 4 758 473.*
9 B. Sun, J. J. Jones, R. P. Burford and M. Skyllas-Kazacos, *J. Electrochem. Soc., 136* (1989) 698–701.

10 M. Skyllas-Kazacos and R. G. Robins, *US Patent No. 55502/86, Australia Patent, Japan Patent Applic.*

11 M. Kazacos and M. Skyllas-Kazacos, *J. Electrochem. Soc.*, *136* (1989) 2759.

12 K. Miyasaha, K. Watanabe, E. Jojima, M. Aida, M. Sumitu and K. Ishikawa, *J. Mater. Sci.*, *17* (1982) 1610–1616.

13 *Tech. Bull. Pigments No. 69*, Degussa Pigments Division, 6000 Frankfurt 1, P.O. Box 2644.

14 *Tech. Bull. Pigments No. 40*, Degussa Pigments Division, 6000 Frankfurt 1, P.O. Box 2644.

15 *Tech. Bull. Pigments No. 62*, Degussa Pigments Division, 6000 Frankfurt 1, P.O. Box 2644.

16 *Tech. Bull. Pigments No. 59*, Degussa Pigments Division, 6000 Frankfurt 1, P.O. Box 2644.

17 S. Zhong, M. Kazacos, R. P. Burford and M. Skyllas-Kazacos, *New Developments in Electrode Material and their Applications*, Wollongong, Australia, Mar. 1990, pp. 276–284.